

METHOD FOR IN-FURNACE REDUCTION FLUE GAS ACIDITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This nonprovisional utility patent application claims the benefit of a prior filed provisional application: 60/544,724 filed February 14, 2004, which is incorporated herein by
5 reference in its entirety.

Background of the Invention

1. Field of the Invention

The present invention relates generally to a method for reducing byproducts emissions from combustion reactions, and, more particularly, to a method for reducing flue
10 gas acidity in combustion furnaces.

2. Description of the Prior Art

Acidity decrease

The flue gas of power generation plants has long been recognized as a source of atmospheric pollution. In the combustion of fossil fuels, some of the naturally present
15 elements are oxidized to form acids, such as SO_3 , NO_x , HCl , HF , and the like. These acids, especially SO_3 , can become a problem if their concentrations exceed certain thresholds. For example, as the SO_3 concentration increases, the acid dewpoint temperature of the flue gas increases. If the temperature of the flue gas is less than the acid dewpoint temperature of the flue gas, the SO_3 in the gas will condense and react with water to form H_2SO_4 , causing
20 corrosion problems inside the furnace. Also, flue gases exiting a furnace cool immediately and SO_3 and other acids in the gas condense, creating localized acid rain, which is the condensation and precipitation of SO_3 and other acids onto the surrounding land with

subsequent corrosion. Excessive SO_3 will condense into small droplets, creating a visible plume as it exits the furnace, which becomes an esthetic and local political problem. If NH_3 -like compounds are present in the flue gas, they can react with SO_3 to form ammonium bisulfate (NH_4HSO_4) which then fouls the air heater.

5 Thus, a need exists to decrease the acid dewpoint temperature of the flue gases such that the acid dewpoint temperature is lower than the flue-gas temperature in the coolest parts of the furnace, such as the ducts and stack. A further need exists to lower the acid content of the flue gases such that the localized acid rain and other problems associated with high-acid flue gas are minimized.

10 SO_3 increase

The particulate matter carried in the flue gas can be removed by electrostatic precipitators that cause the individual particles to accept an electrical charge and then use that charge to attract them to collector plates for disposal. The efficiency of such electrostatic precipitators is dependent upon the ability of the individual particles to take a charge, that is,
15 the resistivity of the particles. It has been found that the presence of SO_3 in the flue gas effectively reduces the resistivity of the particles, making them easier to charge electrostatically.

In the combustion of coal, some of the naturally present sulfur is converted to SO_3 . On the other hand, the effectiveness of SO_3 in reducing the resistivity of the particulate
20 matter in the flue gas depends upon the concentration of the SO_3 , with about 15 to 20 parts per million (ppm) giving optimal results. Therefore, precipitator efficiency is affected by the ability to adjust the amount of SO_3 in the flue gas, regardless of the sulfur content of the coal being burned, to provide an overall SO_3 concentration in the optimal range.

SO₃ is also produced in SCR (catalyst) installations by the oxidation of SO₂ and often exceeds the optimal 15 to 20 ppm optimal concentrations. The catalyst blends typically used in the SCR to reduce NO_x to N₂ (in the presence of ammonia) also oxidize SO₂ to SO₃. The rate of this reaction is strongly temperature dependent and, at higher temperatures, can convert more than 1 percent of SO₂ to SO₃. High sulfur U.S. coal generates anywhere from 2,000 to 3,000 ppm of SO₂ in the boiler, and therefore can result in 20 to 30 ppm of SO₃ out of the SCR. The problem is that as much as 50 percent, or 10 to 15 ppm, of the SO₃ coming out of the SCR will make it past the scrubber and out of the stack. At about 8 to 10 ppm, depending upon the particulate concentration, SO₃ becomes visible as a blue plume.

Furthermore, SO₃ can also be produced catalytically on other boiler surfaces through interaction with elements/chemicals such as Vanadium.

Therefore, because any SO₃ formed prior to the SCR adds to the effluent SO₃, reducing the SO₃ formed prior to the SCR is important for reducing the effluent SO₃ and permits the use of SCR for the reduction of NO_x for gases without generating excessive amounts of SO₃.

SO₃ control

If the SO₃ concentration is too low, the precipitator will operate at less than optimal efficiency. On the other hand, if the SO₃ concentration is too high, the flue gas becomes highly acidic, creating a "blue plume" and contributing to acid rain. In addition, acidic flue gases contribute to corrosion of the pipes carrying the flue gas, and, when combined with NH₃-type chemicals, can clog the air heater.

Furthermore, an SCR is often only intended to be used for six months per year (during the summer ozone control season), and are bypassed during the winter. This creates seasonal variability in the SO₃ concentrations at the precipitator, in the duct work, and out of the exhaust stack.

5 It is therefore desirable to control the concentrations of SO₃ in the flue gas depending upon whether the SCR is in use or not. SO₃ concentrations approaching 40 ppm produce severe adverse local acid problems that are not necessarily regulated, but create local political problems for the facility. The U.S. EPA has indicated that future regulations on SO₃ emissions are to be expected.

10 It is desirable, therefore, to have an SO₃ flue gas system that is capable of adjusting the concentrations of SO₃ in a flue gas with or without an SCR installed to maintain the SO₃ concentration at an optimal level for increased ESP performance, without increased localized SO₃ emissions.

Staging

15 Combustion staging is the process of burning a fuel, i.e., coal, in two or more stages. A fuel-rich stage, or simply, rich stage, is one in which not enough air is available to fully burn the fuel. A fuel-lean stage is one in which there is sufficient or extra air to fully burn the fuel. Staging is used in the prior art to reduce NO_x by a) reducing peak temperatures (thermal NO_x) and b) providing a reducing environment (NO_x reduction). Macro-staging is
20 the dividing of whole sections of a furnace into rich and lean stages and is accomplished through the use of such techniques as Over-Fired Air (OFA). Micro-staging is the creation of proximal microenvironments with functionally different characteristics, such as reduction potential, temperature, and the like. Micro-staging in a furnace can be achieved, for

example, in the first stage of the furnace through the use of Low-NO_x burners with adjustment of spin-vane settings and registers. Increased staging increases the residence time in a reducing atmosphere and increases the effect of the reducing atmosphere.

Prior art has used micro-staging to reduce NO_x emissions in combustion furnaces.

5 Low-NO_x burners (LNB) stage by delivering high-fuel-content primary air into the furnace that mixes with secondary air flowing through one or more secondary air registers. LNB primarily use micro-staging. The flow through a LNB is designed such that the volatile components of the coal mix with the available near-field air at a stoichiometric ratio near unity (1.0), thus anchoring the flame. The net combustion in the central core near the burners
10 is overall fuel rich and does not produce much thermal NO_x, as the temperatures are low. The coal is eventually consumed over the depth of the furnace as more and more air slowly mixes into the central core. The majority of the NO_x created in this region is from the fuel-bound nitrogen reacting to NO through the intermediate HCN. The rate at which the outer secondary air mixes into the core flow is set by the dampers and the spin vanes, as well as the
15 spin vane in the coal pipe. LNB systems decrease NO_x by staging since there is a continuous mixing of the rich products of combustion and secondary air throughout the combustion zone. Staging is increased by decreasing the mixing rate between the rich core flow and the outer secondary air flow.

Prior art has used macro-staging to reduce emissions in combustion furnaces. Macro-
20 staging consists of highly mixed fuel and air in the lower furnace, mixed to a stoichiometric ratio below unity for a large part of the flow. Excess oxygen is ultimately required to assure that all of the fuel has burned and to reduce explosion risks. In a macro-staged furnace, excess air is introduced downstream of the burners. Increased staging is achieved by

increasing the residence time, temperature, or reducing quality of the combustion products in the absence of oxygen.

Prior art used both micro-staging (LNB) and macro-staging (OFA) to reduce NO_x emissions in combustion furnaces. In the case of both micro-staging and macro-staging,
5 components of each of the above are used and adjusted to achieve NO_x emissions reduction.

Staging has nowhere been taught in the prior art for flue gas acidity reduction, acid dewpoint temperature control or SO₃ concentration control in combustion gases.

Summary of the Invention

The present invention is directed to a method for reducing the acidity of flue gases in
10 combustion systems and methods.

The present invention is further directed to a method for reducing the acid dewpoint temperature of flue gases in combustion systems and methods.

It is therefore an aspect of the present invention to provide a method for reducing the acidity of flue gases in combustion systems and methods, including the steps of:

- 15 a) partially combusting the fuel in a first stage to create a reducing environment;
- b) maintaining the reducing environment for a sufficient time period such that reducible acids are reduced to achieve a desirable acidity concentration in the flue gas;
- c) combusting the remainder of the fuel and combustion intermediates in a second stage with oxidizing environment;
- 20 thereby decreasing the acidity of the flue gas by reducing the acid concentration of the gas.

Another aspect of the present invention provides a method for reducing the acid dewpoint temperature of flue gases in combustion systems and methods with staging.

Still another aspect of the present invention provides a method of lowering the acid dewpoint temperature of flue gas, including the steps of:

- a) partially combusting the fuel in a first stage to create a reducing environment;
- b) combusting the remainder of the fuel and combustion intermediates in a second stage with
5 oxidizing environment;
- c) measuring the acid dewpoint of the flue gas;
- d) adjusting the reducing environment for a sufficient time period such that the flue gas acid

Still another aspect of the present invention provides a combustion furnace operated with a method for reducing the acidity of the flue gas, the method steps including:

- 10 a) partially combusting the fuel in a first stage to create a reducing environment;
- b) maintaining the reducing environment for a sufficient time period such that reducible acids are reduced to achieve a desirable acidity concentration in the flue gas;
- c) combusting the remainder of the fuel and combustion intermediates in a second stage with oxidizing environment;
- 15 thereby decreasing the acidity of the flue gas by reducing the acid concentration of the gas.

These and other aspects of the present invention will become apparent to those skilled in the art after a reading of the following description of preferred embodiment(s) when considered with the drawings.

Detailed Description of the Invention

- 20 In the following description, like reference characters designate like or corresponding parts throughout the several views. Also in the following description, it is to be understood that such terms as “forward,” “rearward,” “front,” “back,” “right,” “left,” “upwardly,” “downwardly,” and the like are words of convenience and are not to be construed as limiting

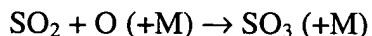
terms. In the present invention, “reducible acid” refers to acids in which the acidity can be reduced or eliminated by the electrochemical reduction of the acid.

The present invention is directed to a method for in-furnace decrease and control of the acid dewpoint temperature using combustion staging. The present invention is further directed to a method for in-furnace reduction and control of SO₃ using combustion staging. Increased staging is advantageously used to simultaneously decrease the acidity, decrease the acid dewpoint temperature and reduce the SO₃ levels of the flue gas.

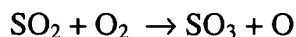
Acidity, acid dewpoint temperature and SO₃ reduction through micro-staging

Similar to how NO_x is reduced back to N₂ in a rich “reducing” environment, SO₃ is reduced back to SO₂ in a reducing environment. With macro-staging, the center of the furnace below the OFA ports is largely fuel-rich. This staged environment can be adjusted to be even less mixed to create reducing micro-stages within the first stage of the furnace. The mixing can be reduced by reducing the spin vane velocity settings of the primary air and coal flow, or additionally or otherwise, the secondary air spin vane and register settings, thus creating reducing micro-stages, or additionally or otherwise, the relative exit velocities between the primary air and coal flow and the secondary air flow can be changed.

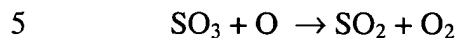
While the majority of fuel-bound sulfur forms SO₂, some forms SO₃ directly during combustion of the fuel-bound sulfur. SO₂ can react to form more SO₃ through the following oxidative reaction:



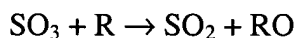
However, this three-body reaction is very slow. An additional source for SO₃ production in an oxidative environment is through the reaction:



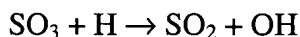
This reaction does not require three bodies to simultaneously collide; however, it is very sensitive to temperature, requiring high temperatures, and it is susceptible to reverse reaction:



None of the above three reactions occur in any significant quantity in a reducing environment due to the lack of O and O₂ species. In a reducing environment, the direct conversion of SO₃ to SO₂ takes place through the following general “reducing” reaction:



10 Where R is any reducing radical species. The primary radical in fossil fuel combustion is the H radical.



Many radicals and molecules can be functional in a reducing environment; e.g., H, OH, C, CO, CH, CH₂, C₂H, CH₃, C_nH_m, N, NH_i, and many others.

15 The above SO₃ reducing reactions are very fast when there are significant concentrations of the reducing radicals (“R”). Sufficient concentrations exist primarily in reducing environments within the first (fuel-rich) stage of the furnace.

In a fuel-rich staged, reducing environment, oxidative chemistry terminates due to greatly decreased (extinguished) concentrations of oxidative combustion species; e.g., OH, O, O₂, HO₂, H₂O₂, and many others. In this environment, species are very competitive for
20 any available oxygen species. Molecules with oxygen atoms that exist in relatively small

concentrations are consumed by oxygen-wanting species that exist in high concentration; e.g., the oxygen in NO is consumed by other species like C, CO, H, and CH. Molecules that have multiple oxygen atoms are particularly at risk; i.e., SO₃ will quickly revert to SO₂ through oxygen abstraction by just about anything around, most notably H atoms.

5 Thus, in a reducing environment, the SO₃ reduction reaction is very fast virtually irreversible while the reducing environment is maintained.

Surprisingly and importantly, with the present invention methods and systems, the net effect is that any SO₃ that is formed during combustion is quickly reduced to SO₂ in the first stage and SO₃ is not reformed by oxidation to SO₂ because there is not enough residence time
10 at sufficiently high temperature in the furnace in the latter, fuel-lean stages. Thus, the present invention advantageously uses the differences in reaction rates to reduce and maintain the SO₃ levels in the flue gas.

Increased staging increases the residence time in a reducing atmosphere, or increases the reducing potential of the atmosphere, to decrease SO₃ concentration and thereby lower
15 the dewpoint temperature. Therefore, to increase the reduction of SO₃, the residence time can be increased or the reducing potential in the flue gases can be increased.

To increase residence time, several methods are available.

- 1) The distance between stages can be lengthened
- 2) The mixing can be increased for macro-staging applications
- 203) The mixing can be decreased for micro-staging applications
- 4) The mass flow between stages can be reduced (deeper staging)
- 5) The volumetric utilization between stages can be increased (e.g., swirl)
- 6) The pressure can be increased

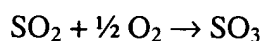
- 7) The density can be increased

To increase the reducing potential in the flue gases, several methods are available.

- 1) The temperature can be increased
- 2) The stoichiometric ratio (i.e., the air-to-fuel ratio) can be decreased.
- 53) The local fuel flow can be increased (for fixed air flow)
- 4) The local air flow can be decreased (for fixed fuel flow)

Mixing within a stage also influences the reduction process. A perfectly mixed stage with a stoichiometric mixture is the best, since these reaction conditions will give the highest temperature, while still maintaining the reducing environment; i.e., minimizing oxidation radicals like O radicals. But, since perfect mixing is impractical, in practice a stoichiometric ratio less than one is used, which minimizes the occurrence of localities with a stoichiometric ratio greater than one. However, as mixing is reduced, a longer residence time and/or higher temperature is needed to achieve a similar reduction of the total acidity, acid dewpoint temperature, and/or SO₃ concentration. However, the temperature of the combustion gases is dependent to a certain extent on the level of mixing, going down if mixing is decreased. Therefore, if an increased temperature is desired for a given degree of mixing, temperature must be increased by other means, such as preheating air, changing heat transfer characteristics of furnace, and the like. Alternatively or additionally, the residence time in the reducing environment can be increased by delaying lean stage air introduction, such as OFA injection.

Note that SO₃ is formed by the oxidation of SO₂ in a catalyst because a catalyst enables the oxidation of SO₂ though the following reaction:



Production of SO_3 in a catalyst is independent of the SO_3 concentration in the gas, since the catalyzed reaction is only dependent on the SO_2 and O_2 concentration. Therefore, any SO_3 that is reduced by the present invention independently reduces the exit SO_3 and is not affected by and does not affect SO_3 production in a catalyst.

5 The present invention thus provides a method for controlling and reducing flue gas acidity, specifically the flue gas concentrations of SO_3 , in order to beneficially (1) affect the efficiency of an electrostatic precipitator, and more particularly, (2) to reduce the concentration of SO_3 and other reducible acids in the flue gas in order to reduce the flue gas acidity and acid dewpoint, thereby reducing air heater pluggage, duct corrosion, and SO_3 emissions to the environment, which can be a source of visible plumes and localized acid rain.

15 In a preferred embodiment of the present invention, macro-staging to regulate furnace acidity and SO_3 levels is achieved through the use of OFA. In another preferred embodiment, micro-staging to regulate furnace acidity and SO_3 levels is achieved through the use of low- NO_x burners. In yet another preferred embodiment, macro-staging and micro-staging through the use of OFA and low- NO_x burners in combination are used to regulate furnace acidity and SO_3 levels. For furnaces with SCRs in operation, the acidity is preferably regulated to reduce total flue gas acidity. For furnaces without SCRs or with by-passed SCRs, the SO_3 is preferably regulated such that the SO_3 levels going to the ESP enhance or favor precipitation. For current ESPs, SO_3 levels between about 10 to about 15 ppm (by volume) in the exhaust is desirable for best ESP efficiency.

20 The dewpoint temperature is a convenient parameter for estimating and/or adjusting the reducing environment variables in order to achieve adequate reduction of acidity and/or

desired SO₃ levels. For a desired level of SO₃ and operating relative humidity, the dewpoint can be determined and the reducing environment variable adjusted accordingly to achieve the desired dewpoint. Other methods of determining acidity and/or SO₃ level can be used for the same purpose without departing from the scope of the invention.

5 In a preferred embodiment of the present invention, a power plant is operated to provide a deeply-staged, micro-stage or macro-stage reducing environment in the lower furnace. The OFA in the upper furnace provides the necessary oxygen to ensure an acceptable level of burnout of the remaining unburned fuel, combustion intermediates, and CO. Additionally, an SCR can be used to reduce NO_x. Thus, an embodiment of the present
10 invention includes a combustion furnace with OFA and low NO_x burners for use with sulfur containing fuels to lower the dewpoint temperature and to reduce the SO₃ concentration.. Additionally, an SCR can be provided to reduce NO_x. The low NO_x burners are preferably of a grade that provides adequate mixing in the primary stage to provide adequate acid dewpoint temperature reducing and SO₃ concentration reduction, thus permitting the use of
15 an SCR, if necessary. Thus, an embodiment of the present invention includes a combustion furnace with high-grade low NO_x burners for the purpose of reducing the flue gas acidity, lowering the acid dewpoint temperature and reducing the flue gas SO₃ concentration. This embodiment can further include an SCR.

 An adequate reducing environment according to the present invention is one that will
20 reduce SO₃ to SO₂ in less than about 2 seconds, more preferably, in less than about 0.5 seconds. In the present invention, such a reducing environment can be achieved when the first stage flue gas temperature is greater than or equal to 900 Kelvin (1160 degrees F), more preferably greater than about 1255 K (1800 degrees F), even more preferably greater than

about 1650 K (2500 degrees F). A reducing environment is one where the ratio of the concentrations of reducing radicals to oxidizing radicals is greater than about 1; more specifically, the ratio of the concentrations of H radicals to O radicals is greater than about 1.

A better reducing environment is one where the ratio of the concentrations of reducing radicals to oxidizing radicals is greater than about 10; more specifically, the ratio of the concentrations of H radicals to O radicals is greater than about 10.

Thus, a method for operating a furnace according to the present invention involves the steps of :

- a) partially combusting the fuel in a first stage to create a reducing environment;
 - 10 b) maintaining the reducing environment for a sufficient time period such that SO_3 is reduced to SO_2 to achieve a desirable level of SO_3 ;
 - c) combusting the remainder of the fuel and combustion intermediates in a second stage with oxidizing environment;
- thereby controlling the levels of SO_3 in the flue gases.

15 Alternatively, in another embodiment according to the present invention, a method of lowering the acid dewpoint temperature of flue gas includes the steps of:

- a) partially combusting the fuel in a first stage to create a reducing environment;
- b) combusting the remainder of the fuel and combustion intermediates in a second stage with oxidizing environment;
- 20 c) measuring the acid dewpoint of the flue gas;

d) adjusting the reducing environment for a sufficient time period such that the flue gas acid dewpoint is lowered to a desirable level;

thereby decreasing the acid dewpoint temperature of the flue gas by reducing the reducible acid concentration of the gas.

5 Examples

The following examples illustrate the results that can be achieved using methods according to the present invention. Methods according to the present invention were used to reduce flue gas acidity and lower acid dewpoint at 3 different power plants. Because SO₃ is the predominant acid in coal furnace emissions, SO₃ emissions were measured and used as an indicator of acidity and dewpoint. The experimental data shown in Tables 1 and 2 were achieved through the use of high-velocity over-fired air and were measured by third-party companies.

Table 1. Effects of Staging Depth on SO₃ levels at 2 different plants.

Parameters	Plant 1		Plant 2	
	Staging Depth			
	Shallow	Deep	Shallow	Deep
Load (MW _{net})	182	179	154	154
NOx (lb/MMBtu)	0.64	0.36	0.63	0.28
Coal %S (%)	1.22	1.22	0.87	0.87
Outlets SO ₂ (ppm)	1100	1100	720	720
Outlet SO ₃ (ppm)	19	5.7	11*	0.5
SO ₃ /SO ₂ (%)	1.7	0.52	1.5*	0.07
SO ₃ Reduction		70%		95%

N/A – Data Not Available; * - Estimated based on assumption that 98.5% of the sulfur in coal goes to SO₂ and 1.5% of the sulfur in coal goes to SO₃.

For the “shallow” staging cases, the over-fired air ports were nearly closed, but still contained cooling flow (around 10% of the total air). For the “mid” staging case, the

over-fired air ports made up nearly 20% of the total air flow. For the “deep” staging cases, the over-fired air ports made up nearly 30% of the total air flow. All three units were corner-fired units and the OFA system was located well above the burner zone.

Table 2. Effect of three levels of staging at a single plant (Plant 3, different from Table 1).

Parameters Load (MW _{net})	Staging depth		
	Shallow	Mid	Deep
	72	72	72
NO _x (lb/MMBtu)	0.56	0.48	0.34
Coal %S (%)	2.85	2.85	2.85
Outlets SO ₂ (ppm)	1856	1855	1856
Outlet SO ₃ (ppm)	5.9	1.9	1.1
SO ₃ /SO ₂ (%)	0.32	0.1	0.06
SO ₃ Reduction (vs Shallow)		68%	81%

Thus, the experimental data demonstrate the ability to regulate the SO₃ level, which is the predominant acid in coal furnace emissions and an indicator of flue gas acidity and acid dewpoint, using methods according to the present invention.

Certain modifications and improvements will occur to those skilled in the art upon a reading of the foregoing description. All modifications and improvements have been deleted herein for the sake of conciseness and readability but are properly within the scope of the following claims.